EXHIBIT 8

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Microbial Dechlorination of Polychlorinated Biphenyls, Dibenzo-*p*-dioxins, and -furans at the Portland Harbor Superfund Site, Oregon, USA

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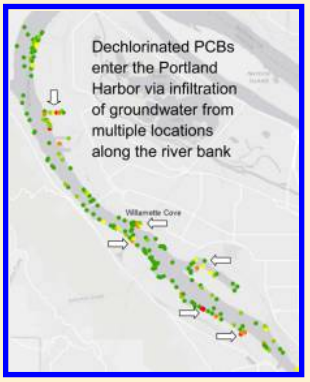
Supporting Information

ABSTRACT: The Portland Harbor (Oregon, USA) has been declared a "Superfund" site because it is impacted by a variety of contaminants, including polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs). Using data collected in the remedial investigation, concentrations of PCBs and PCDD/Fs in sediment and water were examined using positive matrix factorization to look for evidence that PCBs and PCDD/Fs are dechlorinated by anaerobic bacteria. This process has long been known to occur in sediments. Recently, it has been recognized that PCB and PCDD/F dechlorination may also occur in other anaerobic environments, such as in landfills, sewers, and groundwater. The results indicate that a factor related to the dechlorination of PCBs and PCDD/Fs was present in the water but not in the sediment. Spatial patterns in dechlorination products suggest that they come primarily from groundwater. Dechlorination products comprise 22% of the PCBs in the water. The Portland Harbor therefore represents the third major US watershed in which PCBs appear to undergo dechlorination in an environment other than sediment, suggesting that the microbial dechlorination of PCBs and PCDD/Fs is more common than previously assumed. In addition, the Portland Harbor is impacted by PCBs generated inadvertently during the production of pigments, such as PCB 11, which alone exceeded the 64 pg/L federal water quality standard for the sum of PCBs in two of 120 whole water samples.



INTRODUCTION

The Portland Harbor (Oregon, USA) is similar to most of the major harbors of the US in that it is heavily impacted by a variety of contaminants arising from local industry and urbanization, with persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs) being some of the main contaminants.[1] There are over 60 facilities on the harbor that may be sources of contamination.[1] Portland Harbor was placed on the National Priorities List (i.e., "Superfund") in 2000, triggering a large data collection effort. The current study area extends from river mile 1.9 to 11.8, where RM 0 is defined as the confluence of the Willamette and Columbia rivers.

In such a complicated system, source apportionment can be a useful tool to elucidate the main sources of contaminants such as PCBs.[2−4] In addition, source apportionment via factor analysis can identify important processes, including natural attenuation, which might be occurring.[5,6] PCBs and PCDD/Fs are recalcitrant compounds that generally do not degrade in most environments. For PCB and PCDD/F congeners with more than two chlorine substituents, one of the few pathways for their degradation is dechlorination by anaerobic bacteria, which use the chlorinated compound as an electron acceptor for respiration,[7,8] removing some chlorines while leaving the carbon backbone intact. This process is important in the Hudson River, a Superfund site where high levels of PCBs in the river sediment have led to extensive microbial dechlorination.[9] Recently, it has been recognized that microbial dechlorination of PCBs and PCDD/Fs may occur in other anaerobic environments, such as landfills, sewers, and groundwater.[10,11]

The purpose of this study was to examine the available data on PCB and PCDD/F concentrations in water and sediment at the Portland Harbor Superfund site from the Remedial Investigation performed under the supervision of the US EPA in order to identify sources and degradation processes. A second purpose was to compare the sources/processes for PCBs and PCDD/Fs with those observed in two other systems for which a large amount of high quality data is available: the New York/New Jersey Harbor (and associated Hudson River)[6,12] and the Delaware River.[10,13,14]

METHODS

Portland Harbor is a tidal estuary that is home to the City of Portland, Oregon, with a population of about 600 000 (see

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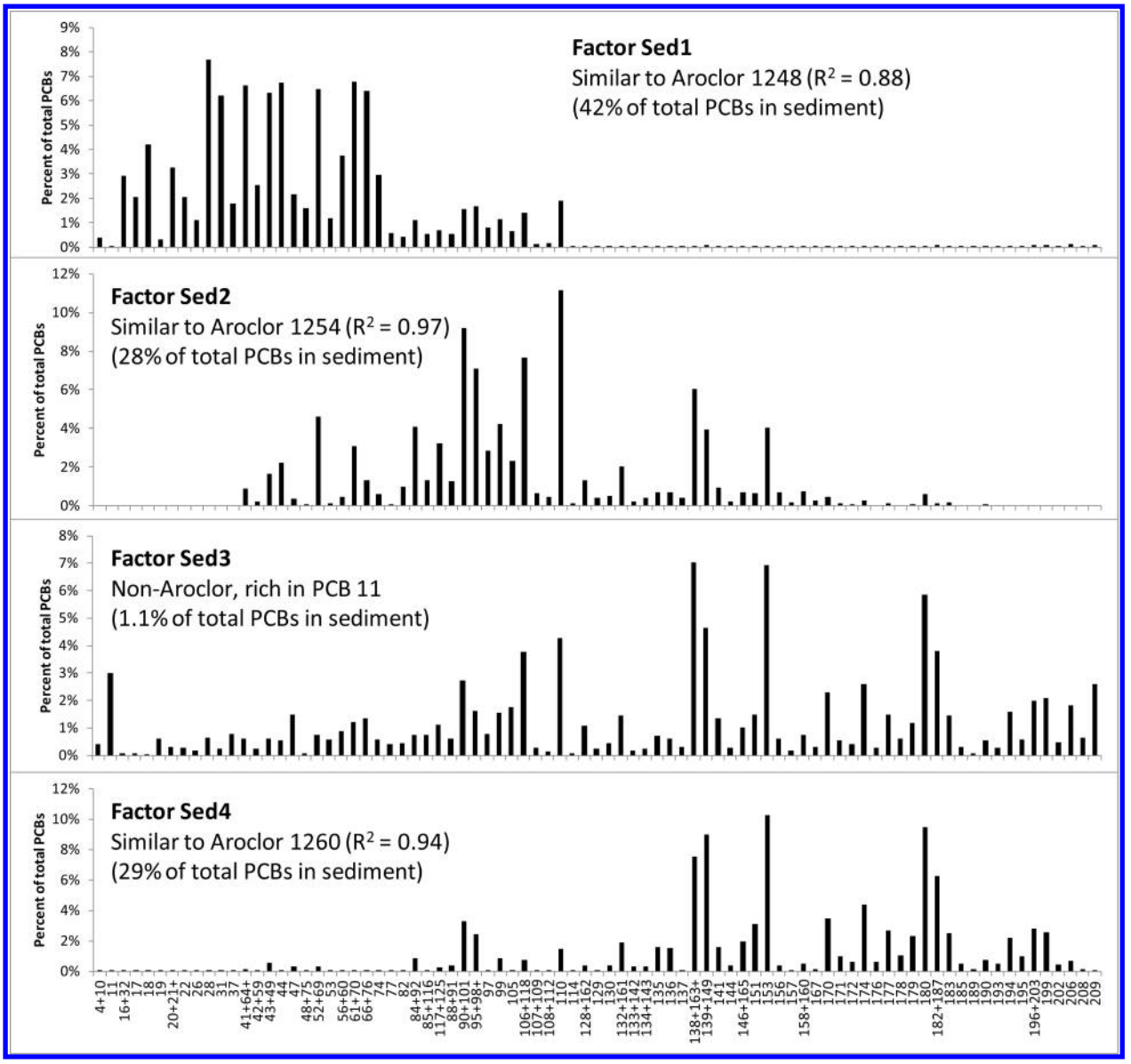

Figure 1. PCB fingerprints from factors derived from PMF analysis on the sediment data set. Co-eluting congeners are labeled using the lowest IUPAC congener number for the first two coeluters. More than two coeluters is indicated with a terminal "+". Complete information about coelutions is provided in Supporting Information, Table S-1. Factors were compared with the Aroclor congener profiles of Rushneck et al.[20]

map, Supporting Information Figure S-1). Water and sediment samples were collected during 2004−2007 under a series of EPA-approved quality assurance project plans associated with the Remedial Investigation of the site. City River water sampling campaigns were designed to capture periods of low flow (less than about 40 000 cubic feet per second (cfs); November 2004, March and July 2005; September 2006), high flow (above 60 000 cfs; January 2006, January through March 2007), and stormwater influenced flow (identified by EPA based on local knowledge and CSO events; November 2006). Figure S-2 of Supporting Information shows the locations of water sampling. Details of sample collection are provided in the quality assurance project plans[15−17] and are summarized in Supporting Information. This and other technical documents related to the site are available at http://yosemite.epa.gov/R10/CLEANUP.NSF/ph/Technical+Documents. Data on concentrations of PCBs and PCDD/Fs in water and sediment at the Portland Harbor Superfund site were obtained primarily via the EPA's STORET database (http://www.epa.gov/storet/). Although the Remedial Investigation (RI) Microsoft Access database was also consulted (provided as Appendix F of ref 1), STORET contained more data (more samples) for PCBs in water than the RI database. The data was checked to ensure that where both sources contained the same samples, the data were identical. The data were examined via the PMF2 software of Paatero and Tapper.[18] The results (especially the best number of factors) were confirmed by running the same data sets using EPA PMF 5.0 (http://www.epa.gov/heasd/research/pmf.html). Because the PMF2 model yielded better agreement between measured and modeled concentrations, the PMF2 results are presented here. Details of PMF procedures, including criteria for determining the best number of factors to adequately describe the data set, are provided in Supporting Information.

A major challenge of using the Portland Harbor Remedial Investigation data lay in the inconsistencies in the analysis of

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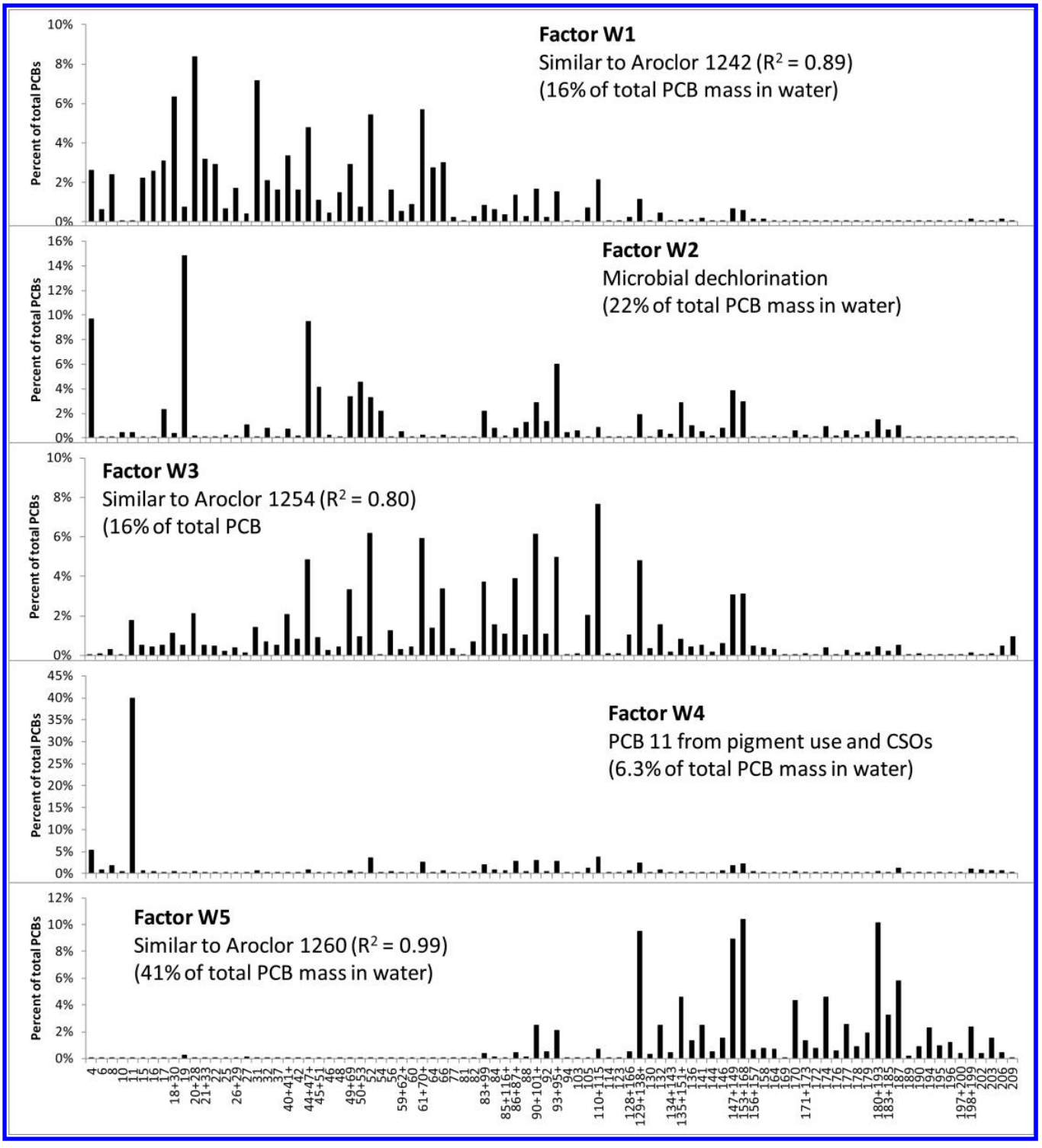

Figure 2. PCB fingerprints from factors derived from PMF analysis on the water data set. Co-eluting congeners are labeled using the lowest IUPAC congener numbers for the first two coeluters. More than two coeluters is indicated with a terminal "+". Complete information about coelutions is provided in Supporting Information, Table S-1. Factors were compared with the Aroclor congener profiles of Rushneck et al.[20] Factors W2 and W4 were attributed to microbial dechlorination and pigment use/CSOs respectively based on arguments described in the text.

PCBs. PCBs were analyzed via EPA method 1668 using two gas chromatography columns (DB-5 and SPB-octyl). Because of their very different coelution patterns, PCB data from these two columns were never combined in any of the data sets for PMF. In general, water samples were analyzed by the lab that used the SPB-octyl column, while sediment samples were sent to laboratories using the DB-5 column, although all laboratories received some of each type of sample. We note that this study design is not optimal and greatly complicates the data management, validation, and use. Generally it is advisible to use one GC column and common reporting formats for all samples in a given study.

Three data sets were examined.

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PCBs in Sediment. PCBs in sediment were measured using the DB-5 (or equivalent) column, on which PCBs 4 and 10 coelute (i.e., they have the same retention time and cannot be quantified separately). This is important because PCB 4 (2−2; numbers before the dash refer to the chlorine positions on ring 1, and the numbers after the dash refer to the chlorine positions on ring 2) is an indicator of microbial dechlorination.[2,3,10,19] After removing samples that were generally nondetect, and congeners (peaks) that were nondetect in most samples, the final data set consisted of 83 peaks (116 congeners or congener groups) in 401 sediment samples. Of these, 1.3% were below detection limit.

PCBs in Water. This data set consisted of PCBs measured separately in the dissolved and particle phases, which we summed to provide "whole water" measurements which were used in the data set. For congeners that were detected in one phase but not both, we set the nondetect congener concentration to zero. For those that were below detection limit in both phases, we used one-half the detection limit of the phase with the lower detection limit as a proxy value. These samples were analyzed using the SPB-octyl column, on which PCB 4 is resolved from PCB 10. The final data set contained 85 peaks (129 congeners or congener groups) in 120 whole water samples, of which 1.1% were below detection limit.

PCBs and PCDD/Fs in Water. The 17 2,3,7,8-substituted PCDD/Fs were measured in 162 water samples (dissolved and particle phases). Whole water concentrations of PCDD/Fs were calculated via the same method used for PCBs. Twelve of the 17 PCDD/F congeners were above detection limit in the majority of samples. Of these 162 samples, PCBs were measured in 78. Thus, the same PCB data used in the data set above were combined with the PCDD/F data for these 78 samples and used in a combined PCDD/F+PCB data set. This data set was then trimmed to 78 analytes by removing PCB congeners that were nondetect in most samples. Thus, the final data set consisted of 12 PCDD/Fs and 65 PCB congeners in 78 samples, of which 1.8% were below detection limit.

RESULTS

Four factors were resolved from the data set of PCBs in sediment (denoted Sed1 through Sed4 in Figure 1). Five factors were resolved from the data set of PCBs in the water (denoted factors W1 through W5 in Figure 2), and seven factors were resolved from the data set of PCBs and PCDD/Fs in the water (denoted factors WD1 through WD7 in Supporting Information Figure S-3). Each of the resolved factors was compared to the Aroclor congener patterns from Rushneck et al.[20] Because a DB-5 column was used for the sediment analysis, the coelution pattern was sufficiently different from the pattern observed by Rushneck et al. (who used an SPB octyl column) that some congeners had to be discarded in the comparison of the factor fingerprint with the Aroclor pattern. For this reason, the assignment of Aroclors to factors is less certain for the sediment data.

PCBs in Sediment. Concentrations of Σ_{209}PCBs in the sediment samples ranged from 0.0045 to 37 000 ng/g (dry weight). The 10th, 50th, and 90th percentile concentrations (the X^{th} percentile concentration is that for which X% of the measured concentrations were lower) were 7.5, 51, and 660 ng/g, respectively. These are somewhat higher than those found in the Delaware River, where the 10th, 50th, and 90th percentile concentrations were 0.66, 11, and 138 ng/g,[14] and lower than in the NY/NY Harbor where concentrations were 71, 630, and 1300 ng/g, respectively.[12] Note that the measurements taken in the NY/NJ Harbor are downstream of the Upper Hudson River and areas such as the Thompson Island Pool, the zone of highest contaminant levels. Most reports state that anaerobic microbial dechlorination of PCBs occurs in deeply buried (anaerobic) sediments that are contaminated with PCBs at levels above about 40 ppm (40 000 ng/g);[21−23] however, microbial dechlorination was also stimulated in sediments with only 2 ppm (2000 ng/g) weathered PCBs.[24] Thus, in all three of these study areas, PCB levels are well below the concentrations often considered necessary to induce microbial dechlorination. The organic carbon content of the sediment of the Portland Harbor ranged from 0.02% to 36%, with a median of 1.7%, similar to the Delaware River, where organic carbon fractions ranged from 0.03% to 7.8% with a median of 1.2%. In the NY/NJ Harbor, organic carbon was measured as total volatile solids. Assuming a conversion factor of 1.8,[25] the estimated organic carbon fraction in the NY/NJ Harbor ranges from 0.2 to 7.8% with a median of 4.2%.

Of the four factors resolved from the data set on PCBs in sediment, three strongly resembled Aroclors and together comprised about 99% of the mass in the sediment (Figure 1). Mass contributions were calculated by dividing the sum of the modeled concentrations of the stated factor in all of the samples by the sum of the modeled concentrations of all factors in all of the samples in the data set. Factor Sed1 resembled Aroclor 1248 (R^2 = 0.88) and comprised 42% of the mass in the data set. This factor explained about 93% of all the PCB 4 + 10 and 19 in the model-predicted concentrations. Factor Sed2 resembled Aroclor 1254 (R^2 = 0.97) and comprised 28% of the mass in the data set. Factor Sed4 resembled Aroclor 1260 (R^2 = 0.94) and comprised 29% of the mass in the data set. Factor Sed3 (Figure 1) contained a high proportion (3.0%) of PCB 11 that was otherwise reasonably well described as a 2:1 mixture of Aroclors 1260 and 1254 (R^2 = 0.85), and comprised 1.1% of the mass in the data set.

What is notable about the sediment data is the lack of any factor related to the microbial dechlorination, despite PCBs 4 + 10, 19, 44, and 47, which are markers for microbial dechlorination, being included in the data set. Since these congeners are also present in Aroclors, their concentrations are explained in the sediment PMF solution solely by factors that resemble Aroclors. Nothing resembling a microbial dechlorination fingerprint emerges even when five or six factors are requested. This is in stark contrast to the Upper Hudson River, where microbial dechlorination of PCBs occurs in sediments, especially in the Thompson Island Pool, and the microbial dechlorination products are still measurable in the water of the Upper New York Harbor (about 0.5 to 2 ng/L, ~10% of total PCBs) nearly 300 km downstream.[6] Although microbial dechlorination products were observed in the discharges to the Delaware River,[10] no microbial dechlorination signal was observed in the sediment or water there.[14]

The agreement between measured and modeled concentrations in the sediment was poor for PCB 4 + 10 (R^2 = 0.38), which is a marker for microbial dechlorination, due to a small number of samples with very high measured concentrations. For example, one of the highest residuals occurred in Willamette Cove, where the measured concentration of PCB 4 + 10 was 38.3 ng/g, while the modeled concentration was 0.445 ng/g. This may indicate that localized microbial dechlorination is occurring, but the extent is not sufficient for the PMF model to isolate it as a separate factor when all the

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data is considered as a single population. These outliers were not located in deep parts of the river channel that are relatively stagnant, nor in deeper layers of the few sediment cores that were collected. Therefore, this discrepancy does not indicate that microbial dechlorination occurs in the sediment. In contrast, the outliers are located on in near-shore sediments (see Supporting Information Figure S-4), suggestingthat the location of the source may be the groundwater which enters via seepage along the river bank. The spatial distribution of the microbial dechlorination products is discussed in more detail below.

PCBs in Water. ΣPCB concentrations in whole water samples from the Portland Harbor were lower than those in the Delaware River and NY/NJ Harbor. They ranged from 0.044 to 12 ng/L. The 10th percentile, median, and 90th percentile concentrations were 0.14, 0.33, and 0.93 ng/L. In comparison, the 10th percentile, median, and 90th percentile concentrations for the Delaware were 0.77, 2.7, and 5.9 ng/L and for the NY/NJ Harbor were 0.72, 7.2, and 26 ng/L, respectively.

Of the five factors resolved from the data set on PCBs in the water, factor W1 resembled Aroclor 1242 (R^2 = 0.89), factor W3 resembled Aroclor 1254 (R^2 = 0.80) and factor W5 resembled Aroclor 1260 (R^2 = 0.99) (Supporting Information Figure S-2). These factors constituted 16%, 16%, and 41% of the mass in the data set, respectively. Thus, collectively, relatively unweathered Aroclors comprise about 72% of the PCBs in the water. More detailed discussion of Aroclor patterns in water versus sediment can be found in the Supporting Information.

Factor W4 (Figure 2) was rich in PCB 11 (40% of total PCBs in that factor). Even when PCB 11 was removed, this factor did not resemble any of the Aroclors. PCB 11 is known to be present as an inadvertent byproduct in pigments that are used in consumer goods such as printed paper and clothing, as well as paint.[26−30] PCB 11 is produced during incineration along with coplanar congeners, such as PCBs 77, 105, 114, 169, and 189.[31] It is unlikely that the PCB 11 in factor W4 arises from incineration, because these coplanar congeners are not present in factor W4 and the closest incinerator in the EPA's directory of municipal and industrial incinerators is more than 50 km north (not generally upwind) in Kalama, WA. In addition, factor W4 constituted 6.3% of the mass in the water under all flow regimes, but 16% of mass under stormwater influenced flow conditions, and only 3−6% under other flow regimes. If it were associated with atmospheric deposition from incineration, concentrations of this factor would not increase under stormwater influenced flow. In previous work, we surmised that the factor dominated by PCB 11 in the Delaware River[5] and NY/NJ Harbor[6] was related to stormwater, treated wastewater discharges, and combined sewer overflows, based on its prevalence during high flow events (see S-6 for a comparison of the PCB 11 dominated factors from these three systems). Thus, it appears that factor W4 is similarly related to stormwater and possibly also combined sewer overflows in Portland Harbor. PCB 11 concentrations ranged from 1.7 to 78 pg/L, with 10th, 50th, and 90th percentile concentrations of 5.3, 22, and 47 pg/L. In two samples, the PCB 11 concentration alone was greater than the 64 pg/L federal water quality standard for Σ_{209}PCBs. This information adds to the growing body of evidence that PCB 11, which enters the environment primarily through the use of various organic pigments, is a significant environmental concern.[26,27]

Factor W2 (Figure 2) represents microbial dechlorination. This interpretation is based on the congener fingerprint, which was dominated by PCB 4 (10% of total PCBs) and PCB 19 (15%), and contained reasonably high proportions of PCBs 44(23−25)+47(24−24)+65(2356) (9%) and PCBs 45(236−2)+51(24−26) (4%). All of these congeners are known to be markers of the microbial dechlorination of PCBs by bacteria under anaerobic conditions.[2,3,10,19] We know of no other processes that could produce such a fingerprint. A comparison of the congener patterns of the various microbial dechlorination factors observed in the three watersheds is shown in Supporting Information, Figure S-5. In the Delaware dischargers[10] and the NY/NJ Harbor dischargers[11] data, two microbial dechlorination factors were observed. The "advanced" microbial dechlorination factor was dominated by PCBs 4 and 19 and was most closely associated with combined sewers, groundwater, and landfills. In contrast, the "partial" microbial dechlorination factor was dominated by PCBs 44+47+65 and PCBs 45+51 and was most closely associated with separate sanitary sewers. In contrast, only one microbial dechlorination factor was observed in the water of the NY/NJ Harbor.[6] Thus, the absence of a partial microbial dechlorination factor in Portland Harbor is not surprising, since any separate sewers in the region lead to the Columbia Boulevard Treatment Plant, which discharges into the Columbia River, not the Portland Harbor.

Factor W2 comprised 22% of the mass of PCBs in the Portland Harbor water data set. In comparison, concentrations of the equivalent microbial dechlorination factor were around 17−42 ng/L (58−89% of the sum of PCBs) in the water in the Upper Hudson River,[6] where extensive microbial dechlorination of PCBs occurs in the sediments. In the Delaware River, about 19% of the PCBs in the effluents from point dischargers consisted of dechlorinated PCBs, but the microbial dechlorination signal was not discernible in the water. Factor W2 contains only 0.1% PCB 11. The microbial dechlorination factor in the Delaware River dischargers similarly contained virtually no PCB 11.[10] Since microbes generally remove chlorines at the meta and para, but not ortho, positions, PCB 11 is probably only produced from the dechlorination of non-ortho-substituted PCB congeners. The most likely parent compounds of hypothetically- microbially produced PCB11 would be PCB 37(34−4), PCB 77(34−34), and PCB 81(345−4), none of which are present in any significant amount in factor W2, or in the Aroclors. This suggests that PCB 11 is not associated with the microbial dechlorination of PCBs. Also, it suggests that the microbial dechlorination happening in the Portland Harbor is not closely associated with wastewater collection and treatment, since these types of sources would tend to contain PCB 11.

In the microbial dechlorination signals from the NY/NJ Harbor water[6] and Delaware River dischargers,[10] PCB 4(2−2) was more abundant than PCB 19(26−2). The ratio of PCB 4 to PCB 19 was 1.97 in the Delaware dischargers and 3.65 in the NY/NJ Harbor. In contrast, in Portland Harbor, PCB 19 was more abundant that PCB 4 and the 4/19 ratio was 0.65. While a few strains of bacteria have been identified that can remove chlorines at the ortho positions,[32,33] generally this is not observed in natural systems. According to the Aroclor compositions measured by Rushneck et al.,[20] if chlorines in the ortho position are not removed, the final 4/19 ratio would be greater than one for all Aroclors with 54% or less chlorine content (i.e., Aroclors 1016, 1242, 1248, and 1254). The only widely used Aroclor that could produce a 4/19 ratio less than

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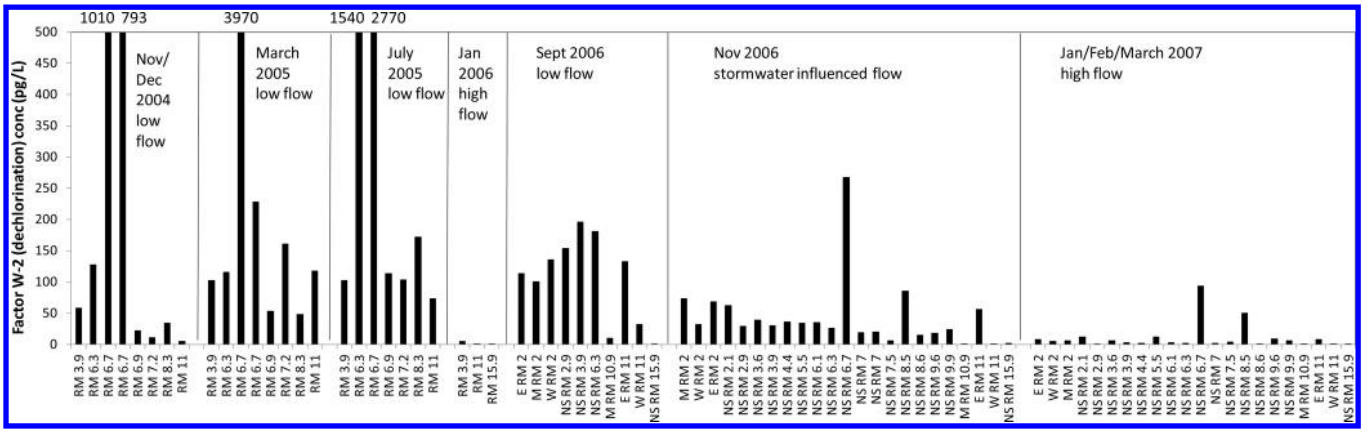

Figure 3. Concentrations of factor W2 (PCB dechlorination) in select water samples. Concentrations that are off scale are indicated above the bar. *X*-axis labels refer to river mile (RM) at which each sample was collected. E = east side of the river, M = middle, W = west. Unless NS (near surface) is indicated, all samples were vertically integrated. See Supporting Information Figure S-2 for a map of sampling locations.

one is Aroclor 1260, which was the most abundant Aroclor in the Portland Harbor PMF solution. In fact, if only congeners with six or more chlorines are included in the comparison, factor W2 resembles Aroclor 1260 (R^2 = 0.70). No other Aroclor has such high proportions of PCBs 147, 153, 180, and 187. This suggests that the partially dechlorinated PCBs in Portland harbor water originated as A1260.

PCBs and PCDD/Fs in Water. Examination of the combined data set on PCBs and PCDD/Fs in water yielded a factor that contained high proportions of PCB 4 (25%) and PCB 19 (37%) and thus represents dechlorination (Supporting Information Figure S-3). The PCDD/F portion of this fingerprint likewise contained congeners associated with microbial dechlorination, but this factor only accounted for 0.8% of the PCDD/F mass in the data set. Therefore, detailed discussion of these results is provided in Supporting Information.

Spatial and Temporal Variation in Microbial Dechlorination Products. The PMF results suggest that both PCDD/Fs and PCBs are dechlorinated in the Portland Harbor watershed, but that this microbial dechlorination does not occur in the sediment. Where does it occur? We can rule out several possible sources. The spatial variation in factor W2 concentration (Figure 3) is not consistent with a source upstream. Our previous work[10,11] demonstrated that PCBs and PCDD/Fs can undergo extensive microbial dechlorination in landfills, sewer systems (especially combined sewers), and groundwater. There are no landfills or treated sewage outfalls in the study area. Portland does have combined sewers with 55 outfalls spread along the length of the Superfund site, but the City has implemented a series of control measures. Some of these were in place during the entire sampling period, and by December 1, 2006 the west side CSO tunnel was completed, reducing CSO flows by over 90% from the 1990s baseline. According to City records, the maximum possible contribution of CSOs to the river flow at Portland during the 1990s would have been 0.15%, and would have been much lower during the study period when some CSO controls were already in place. A couple of other factors suggest that CSOs are not a major source of factor W2. As noted above, if the microbial dechlorination signal were associated with wastewater, it would likely contain a higher fraction of PCB 11. Also, if CSOs were an important source of W2, the microbial dechlorination signal would be highest near clusters of CSO outfalls. It would also be most abundant under stormwater influenced flow. Figure 3 demonstrates that this is not the case.

This leaves microbial dechlorination in groundwater as a likely source of factor W2. Several other factors suggest that groundwater is the source. First, factor W2 was most abundant at low flow conditions (averaging 22% of total PCBs) versus just 9% under stormwater influenced flow and 4% under high flow conditions. Second, during most sampling campaigns, the concentrations of factor W2 are highest around river mile 6.7, in an area known as Willamette Cove, where there are no CSO outfalls (Supporting Information Figure S-2 shows the water sampling locations). Concentrations at this location are highest under low flow conditions, but are noticeably elevated even under high and stormwater influenced flow, suggesting that they are associated with groundwater inputs, not CSOs. Willamette Cove is the site of an old shipbuilding/repair and drydock facility as well as a lumber mill, plywood mill, and barrel manufacturing site. This site is known to contain PCBs and PCDD/Fs in soils, groundwater and beach sand, and an oily sheen was noted on the groundwater and the surface water at this location during a visual inspection in 2011 (http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?seqnbr=2066). In Willamette Cove (RM 6.7), concentrations of factors W2 (microbial dechlorination) and W5 (Aroclor 1260) are strongly correlated (R^2 = 0.99, n = 9), in large part because these two factors comprise 64−100% of the PCBs in these samples.

Third, the PCB 4 + 10 residuals in the sediment (Supporting Information Figure S-4) suggest that PCB microbial dechlorination products enter the river at a number of discrete locations along the river's banks. These are clustered in Willamette Cove and the Swan Island basin, in agreement with the water results. However, the PCB 4 residual in the sediment is also high in the near-shore sediments near Schnitzer Steel, Oregon Steel Mills, Terminal 2, Gunderson and the Texaco Terminal and Dock, and Siltronic. Many of these sites housed ship building, repair, or breaking facilities at one time, especially during World War II (http://www.shipbuildinghistory.com/history/shipbuilders.htm). In addition, all of these areas have CSO outfalls. However, PCB microbial dechlorination products are not present near many of the other CSO outfalls. This implies that microbial dechlorination either occurs in some but not all combined sewers in the area, or in a few discrete locations in groundwater.

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In the Delaware River, evidence for microbial dechlorination of PCBs in groundwater was observed in the effluent from 17 different sites, including seven of nine sites with known contaminated groundwater that had been listed under either the state remediation programs or the Superfund.[10] These include the only steel mill and the only shipyard in the Delaware River discharger database. The advanced microbial dechlorination factor accounted for as much as 67% of the PCBs discharged (via pumped groundwater) at the former US Steel plant in Fairless Hills, PA.[10] Effluent from the former Philadelphia Naval Shipyard contained high levels of dechlorinated PCBs ranging from 0.28 to 8.4 ng/L (averaging 31% of total PCBs).[10] Like Willamette Cove, where Aroclor 1260 comprises an average of 51% of the sum of PCBs, the Philadelphia Naval Shipyard effluent also contained high proportions of Aroclor 1260 (an average of 30% of total PCBs).

The final reason that microbial dechlorination in groundwater is the most likely source of factor W2 is that groundwater flow into the Portland Harbor is extensive and rapid.[34] The hydrogeology of the Portland Harbor is characterized by three aquifers, all formed from alluvial sediments. The Harbor area is located downstream of a decline in gradient that has made it a depositional site since the early Pliocene.[35,36] The resulting fine-grained sedimentary rocks became the Troutdale Formation where interbedded confining units created two confined aquifers.[36] During the Pleistocene, there was a braided channel in what later became harbor area, leaving deposits of interbedded gravels and sands of up to 50 m thick. These deposits form an unconfined, unconsolidated aquifer where flow gradients are predominantly horizontal. Overlying this aquifer are silt, sand, and gravel derived from late-glacial Missoula floods.[37] Missoula floods deposits reach up to 300 feet thick and form the highly permeable uppermost unconfined aquifer.[36] The Willamette River has incised into these deposits in many places. Hydraulic conductivity in the upper, unconfined aquifer has a median value of 60 m per day with a high degree of variability depending on well location. Spring and seep discharge rates also vary with the rate of aquifer pumping, and a number of springs have reduced in discharge with population growth and an associated increase in the number of pumping wells. Median hydraulic conductivities are similar for the intermediary and Troutdale aquifers, ranging between 2 and 5 m per day.[38]

The connection between the upper, unconfined aquifer and the waters in Portland Harbor is maintained through seeps on the harbor bed, as most streams in the Portland Basin gain water from the aquifers underlying channel beds.[38] The regional groundwater gradient drives discharge into the harbor, and seep flow from the aquifer to the harbor varies in rate with season and tide. The uppermost, unconfined aquifer has a strong connection to surface water, fluctuating in saturated thickness seasonally and with a diurnal tidal fluctuation of up to 1 m per day. Local permeability of the underlying aquifer and the hydraulic gradient between the aquifer and river stage drive the hydraulic conductivity and discharge rate from the aquifer to the overlying river and harbor waters.

Thus, we conclude that the major source of factor W2 is groundwater from contaminated sites, while CSOs may also contribute. If correct, this conclusion suggests that controlling contaminant levels in groundwater flowing into the river will be important in reducing PCB levels in Portland Harbor, although the other inputs, including the legacy contamination in the sediment, are also important sources of PCBs to the Portland Harbor.

Implications. This investigation revealed that Portland Harbor, like the NY/NJ Harbor and the Delaware River, is impacted by PCB 11 generated inadvertently during production of organic pigments and dispersed throughout the environment by the use of such pigments in printed material, paints, etc.[26,27,29] Various data sources suggest that many other US waterways are impacted by PCBs from pigments, including the Santa Fe and Rio Grande Rivers in New Mexico (STORET), San Francisco Bay (California Environmental Data Exchange Network; http://www.ceden.org/), and the Houston Ship Canal (Houston, TX).[39]

In addition, investigations in three watersheds on both the east and west coasts of the US have now found evidence of microbial dechlorination of PCBs in compartments other than sediment, including groundwater, landfills, and sewers. The evidence is thus building that microbial dechlorination of PCBs is much more common than previously assumed. In addition to PCBs, evidence now suggests that PCDD/Fs are dechlorinated (presumably by bacteria) in sewers and landfills in the NY/NJ Harbor[11] and in groundwater in the Portland Harbor.

The accumulation of large data sets and access to those data sets via portals such as STORET has made these kinds of investigations possible. As data continues to accumulate, this type of data mining activity would be greatly aided by common methodology and reporting formats. The present study was hampered by inconsistencies in the PCB data that originate in a general lack of understanding about the specifics of the 1668 method and about the management of this kind of analytical data. Similar problems were encountered in the data from the CARP, where New York and New Jersey used two different columns for PCB analysis.[11] In the Delaware River, the Delaware River Basin Commission (DRBC) developed a set of modifications and instructions on the application of method 1668 that allowed the accumulation of a homogeneous data set across sediment, water, and biota, with samples collected by 100 dischargers and analyzed by at least 5 different contract laboratories, in a project overseen by three states and two EPA regions. These modifications are available at http://www.state.nj.us/drbc/quality/toxics/pcbs/monitoring.html. We suggest that the EPA and other organizations should prioritize better data management including the reporting of metadata such as detection limits and surrogate recoveries, and that all agencies should adopt DRBC's protocols for method 1668.

■ ASSOCIATED CONTENT

Supporting Information

Background on sampling and modeling, as well as maps and fingerprint information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01092.

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Notes

The authors declare no competing financial interest.

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Microbial dechlorination of polychlorinated biphenyls, dibenzo-p-dioxins, and -furans at the Portland Harbor superfund site, Oregon, USA

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Supporting information

Thirteen pages

Six figures

Two tables

Figure S-1. Map of Portland Harbor superfund site showing major known contaminated sites.

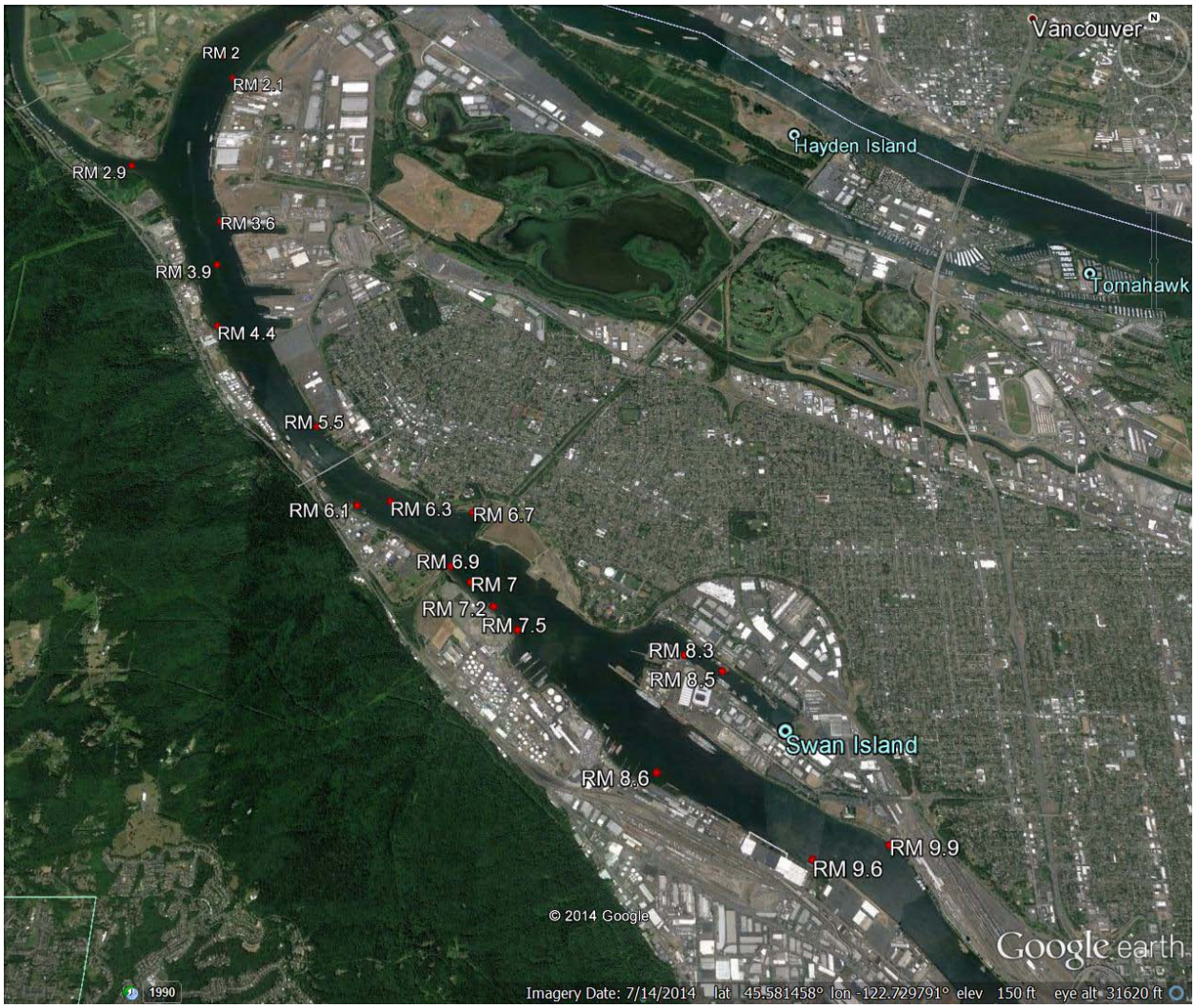

Figure S-2. Map of Portland Harbor showing water sampling sites labeled by river mile (RM). Upstream sites at RM 11 and 15.9 are not included due to map scale. Map drawn with Google earth.

Table S-1. List of congeners used in PMF modeling and coelution patterns.

Sediment (DB-5 column)		Water column (SPB-octyl column)		
PCB4+10	PCB129	PCB 4	PCB 88	PCB 197+200
PCB11	PCB130	PCB 6	PCB 90+101+113	PCB 198+199
PCB16+32	PCB132+161	PCB 8	PCB 92	PCB 202
PCB17	PCB133+142	PCB 10	PCB 95+100+93+102+98	PCB 203
PCB18	PCB134+143	PCB 11	PCB 94	PCB 206
PCB19	PCB135	PCB 15	PCB 103	PCB 209
PCB20+21+33	PCB136	PCB 16	PCB 105	
PCB22	PCB137	PCB 17	PCB 110+115	
PCB26	PCB138+163+164	PCB 18+30	PCB 114	
PCB28	PCB139+149	PCB 19	PCB 123	
PCB31	PCB141	PCB 20+28	PCB 128+166	
PCB37	PCB144	PCB 21+33	PCB 138+163+129+160	
PCB41+64+71+72	PCB146+165	PCB 22	PCB 130	
PCB42+59	PCB151	PCB 25	PCB 132	
PCB43+49	PCB153	PCB 26+29	PCB 134+143	
PCB44	PCB156	PCB 27	PCB 151+135+154	
PCB47	PCB157	PCB 31	PCB 136	
PCB48+75	PCB158+160	PCB 32	PCB 141	
PCB52+69	PCB167	PCB 37	PCB 144	
PCB53	PCB170	PCB 40+41+71	PCB 146	
PCB56+60	PCB171	PCB 42	PCB 147+149	
PCB61+70	PCB172	PCB 44+65+47	PCB 153+168	
PCB66+76	PCB174	PCB 45+51	PCB 156+157	
PCB74	PCB176	PCB 46	PCB 158	
PCB77	PCB177	PCB 48	PCB 164	
PCB82	PCB178	PCB 49+69	PCB 169	
PCB84+92	PCB179	PCB 50+53	PCB 170	
PCB85+116	PCB180	PCB 52	PCB 171+173	
PCB87+117+125	PCB182+187	PCB 54	PCB 172	
PCB88+91	PCB183	PCB 56	PCB 174	
PCB90+101	PCB185	PCB 59+62+75	PCB 176	
PCB95+98+102	PCB189	PCB 60	PCB 177	
PCB97	PCB190	PCB 61+70+76+74	PCB 178	
PCB99	PCB193	PCB 64	PCB 179	
PCB105	PCB194	PCB 66	PCB 180+193	
PCB106+118	PCB195	PCB 77	PCB 183+185	
PCB107+109	PCB196+203	PCB 81	PCB 187	
PCB108+112	PCB199	PCB 82	PCB 189	
PCB110	PCB202	PCB 83+99	PCB 190	
PCB114	PCB206	PCB 84	PCB 194	
PCB128+162	PCB208	PCB 117+116+85	PCB 195	
	PCB209	PCB 108+119+86+97+125+87	PCB 196	

Dataset details

Surface sediment and beach sediment samples were collected at 276 locations with either a handheld coring device (subaerial beaches), small dredge sampler (shallow water beaches), or power grab sampler (river channel and river nearshore areas), and sediment cores were collected with a vibracoring device. Sediment samples were analyzed for PCB and PCDD/Fs (and many other contaminants not discussed here) as well as total organic carbon. River water samples (about 400 L each) were collected at 94 locations using an Infiltrex 300 pump system (Axys Analytical Services). Particles were retained on a 0.5-µm glass fiber filter. Dissolved phase contaminants were collected on a column of XAD-2 resin. All 209 PCB congeners were measured using EPA method 1668 (revision not specified), and the 17 2,3,7,8-substituted PCDD/Fs were measured via EPA method 1614.

PMF details

A major challenge in using this data was the absence of surrogate recoveries and sparse information about limits of detection (LOD), both of which are needed to construct accurate input matrices for PMF analysis. Where concentrations were below detection limit, the LOD was reported instead of the measured concentration in STORET but not in the RI database. Thus for the LOD matrixes for PMF analysis, the limited data on LODs were used to reconstruct what the LODs must have been for congeners that were detected, based on the assumption that LODs were the same for all congeners in a homologue in any given sample. In the concentration matrix, concentrations that were below detection limit were replaced with one-half of the inferred detection limit.[1] There are many different ways to treat data that is below the LOD, but our experience suggests that the choice to replace non-detect data with one-half the LOD (versus for example a random number between zero and the detection limit) has virtually no effect on the PMF solution when the number of data points that are below detection is small, as in all three datasets examined here. LODs ranged from 0.1 to 358 pg/g for PCBs in sediment, from 0.00020 to 1.4 pg/L for PCBs in the water column, and from 0.00064 to 3.5 pg/L for PCDD/Fs in water.

The uncertainty matrix is usually constructed from the relative standard deviation of the percent recoveries of the surrogate that is applied to each analyte. In the total absence of surrogate recovery information, the uncertainty matrix was borrowed from previous studies that used the same analytical methods and the same matrixes i.e. Du et al. [2] for the water column PCBs, Rodenburg et al.[3] for the water column PCDD/Fs, and Praipipat et al. [4] for the sediment PCBs. Note that uncertainties are input as a fraction for the PMF2 software, but as absolute concentrations in the PMF 5.0 software.

Justification for selection of the number of factors

PCBs in sediment

PMF2: Three, four, five, and six factor solutions were generated. The four factor model was selected. For the four-factor model, all nine seed runs were similar with an RSD of the G matrix of 1.8%. All four of these factors had positive and significant coefficients when the G matrix was regressed against the measured sum of PCBs. In contrast, this regression for the five-factor model revealed one factor with a coefficient that was not significant. Also, for the five factor model, two of the nine seed runs were very different from the other seven. The G-space plots indicated that all factors of the four-factor solution were independent of each other. The agreement (R^2) between measured and modeled concentrations was greater than 0.77 for 80 of 83 peaks. The three peaks/congeners with low R^2 were PCB 206 (0.38), PCB (0.34) and PCB 209 (0.53). However, the good agreement between measured and modeled concentrations for PCBs 4+10 and 19 (which are markers of dechlorination) were driven by the two data

points with the highest concentrations of these congeners, both collected at RM 8.8. When these two samples are discarded, the agreement between measured and modeled concentrations is much worse for these congeners due to several outliers with high measured concentrations.

PMF 5.0: Bootstrapping of the 4- and 5-factor models confirmed that 4 was the best number of factors. Out of 100 bootstrap runs, at least 86 mapped correctly when 5 factors were requested. When 6 factors were requested, the new factor was 'smeared' across five of the six factors, with 21, 4, 24, 6 and 1 of the bootstrap runs mapped across the five. This indicates that the new factor was not meaningful.

PCBs in water column

PMF2: Four, five, six, and seven factor solutions were generated. The five factor model was selected. The five factor solution had low RSD of the G matrix (0.43%). The six factor model had two outliers among the nine seed runs. Although both the five and six factor models gave positive and significant coefficients for all factors when the G matrixes were regressed against the measured sum of PCBs, two of the factors in the six-factor model were similar in fingerprint (both resembled Aroclor 1260). Therefore the five factor model was selected. The agreement (R^2) between measured and modeled concentrations was greater than 0.7 for 85 of 90 peaks. The peaks/congeners that were not well modeled were PCB 11 (R^2 = 0.51), PCB 81 (0.24), PCB 123 (0.18), PCB 169 (0.027), and PCB 209 (0.40). Note that PCBs 81, 123, and 169 were included in the data matrix despite low concentrations because they are dioxin-like congeners. The G space plots for the five factor model showed strong correlation between factors W2 and W5, but this was because the regression was dominated by the seven samples with the highest PCB concentrations, all of which were collected at Willamette Cove. When the nine samples collected at Willamette Cove were removed, all of the factors were independent of each other.

PMF 5.0: Bootstrapping of the 5- and 6-factor models confirmed that 5 was the correct number of factors. Out of 100 bootstrap runs, at least 92 mapped correctly when 5 factors were requested. When 6 factors were requested, the new factor was 'smeared' across four of the six factors, with 6, 37, 42, and 1 of the bootstrap runs mapped across the four, and 14 'unmapped' runs. This indicates that the new factor was not meaningful. For the 5-factor model, 74 of the 90 congeners were modeled more accurately by the PMF2 model. The same five congeners (R^2) were not well modeled by PMF 5.0: PCB 11 (R^2 = 0.31), PCB 81 (0.27), PCB 123 (0.21), PCB 169 (0.088), and PCB 209 (0.31). However, two additional congeners were not well modeled by PMF 5.0: PCB 6 (R^2 = 0.42 via PMF 5.0 vs. 0.84 via PMF2), PCB 8 (0.17 vs. 0.94).

PCBs and PCDD/Fs in the water column

PMF2: Four, five, six, seven, and eight factor solutions were generated. The seven factor model was selected. The six and eight factor models did not converge on a robust solution, with the nine seed runs generating at least three distinct solutions. In contrast, for the seven factor solution, eight of the nine seed runs were in good agreement with each other (RSD of the G matrix = 1.4%). All seven factors yielded positive and significant coefficients in the regression of the G matrix versus the sum of analytes, and all seven were independent of each other. The agreement between measured and modeled concentrations (R^2) was greater than 0.7 for 73 of 77 analytes. Analytes with low R^2 values were 1,2,3,7,8,9-HxCDD, 1,2,3,7,8-PCDD, and 2,3,4,6,7,8-HxCDF, all of which had R^2 values greater than 0.65, and PCB 126, a dioxin-like congener. As with the solution for PCBs in the water column, the seven factors were independent of each other when the nine samples from Willamette Cove were excluded.

PMF 5.0: PMF 5.0 was not able to generate a useful solution for this data set. When the original uncertainty matrix was used, none of the base runs converged on a solution. The PMF 5.0 User Guide[5] suggests that this might be caused by underestimation of uncertainty, so the uncertainty matrix was increased by 50% for all data points. With this higher uncertainty, a small number (perhaps 4 out of 20) of the base runs converged when 3 to 6 factors were requested, but none converged when 7 factors were requested. Despite the fact that PMF 5.0 could not corroborate the PMF2 results, the PMF2 results were deemed reliable because the PCB portion of each factor resembled one of the factors generated by the PCB-only data matrix above.

Comparison of Aroclor patterns in water and sediment

There is a surprising mismatch between the inferred Aroclor abundances in water and sediment (Table S-2). In sediment, factors resembling Aroclors 1248, 1254, and 1260 were observed, but in the water column, factors resembling Aroclors 1242, 1254, and 1260 were observed. It is possible that factor W1 which resembles Aroclor 1242 (R^2 = 0.89) represents the dissolved fraction of factor Sed1, which resembled Aroclor 1248 (R^2 = 0.88). Recall that the sediment data utilized a DB-5 column, so the correlation between the factor Sed1 and the Aroclor is less certain. Overall, it seems that even when method 1668 is used and the data set is of high quality, it is difficult to discern between low molecular weight Aroclors such as 1016, 1242, and 1248. If we conclude that factors W1 and Sed1 are related to the same source, i.e. low molecular weight Aroclors, this suggests that this low-molecular weight Aroclor signal is more abundant in the sediment than the water column. This is in contrast to our previous work in the Delaware River[4], where we found that low molecular weight Aroclors were relatively more abundant in the water than the sediment. In contrast, in the Portland Harbor we find that the high molecular weight Aroclor 1260 is proportionately more important in the water than the sediment.

Table S-2. Relative abundance of factors resembling Aroclors in sediment vs. water at low, high, and stormwater-influenced flow.

		A1242	A1248	A1254	A1260
Water:					
Factor ID		W1	none	W3	W5
flow condition	**low**	17%	~0%	24%	29%
	high	24%	~0%	32%	31%
	stormwater-influenced	27%	~0%	23%	21%
Sediment:					
Factor ID		none	Sed1	Sed2	Sed4
		~0%	42%	28%	29%

Results from PMF examination of PCBs and PCDD/Fs in water

The combined data set containing both PCBs and PCDD/Fs was examined primarily to determine whether PCDD/Fs were also being dechlorinated. This approach was used in previous work,[3] and is based on the assumption that microbial dechlorination of both classes (PCBs and PCDD/Fs) occurs in the same locations due to anaerobic conditions. The results of the PMFwere not particularly useful for the apportionment of PCCD/F and/or PCB sources because neither all of the major PCB congeners, nor all of the 17 PCDD/Fs were included in the dataset. In addition, it is well known that compounds that have

high concentrations in all samples, such as OCDD, are difficult to model via factor analysis.[6-8] Thus detailed presentation of the PMF results from the PCB+PCCD/F data set can be found in figure S-3. Factor WD3 contains high proportions of PCB 4 (25%) and PCB 19 (37%) and thus represents microbial dechlorination. Because OCDD typically dominates the concentrations of PCDD/Fs in the environment, it is expected to be present in all of the WD factors.[6-8] In all of the other WD factors, the PCDD/F portion is indeed dominated by OCDD (at least 78% of Σ_{12}PCCD/Fs). In contrast, in factor WD3, OCDD is just 16% of the Σ_{12}PCDD/Fs and the factor is instead dominated by 1,2,3,4,6,7,8-HpCDD (73% of Σ_{12}PCDD/Fs). Other PCDD/F congeners that are abundant in factor WD3 are 1,2,3,4,6,7,8-HpCDF, 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF, all of which have been associated with microbial dechlorination in various studies.[8-10] In our previous report on the microbial dechlorination of PCDD/Fs in sewers and landfills,[3] OCDD was similarly absent, 1,2,3,4,6,7,8-HpCDD was dominant, and 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF were abundant in the factor that contained high proportions of PCB microbial dechlorination products. This pattern therefore appears to represent microbial dechlorination of PCDD/Fs. However it must be noted that factor WD3 explains only 0.8% of the PCDD/F mass in the dataset. Thus the fingerprint of this factor suggests that microbial dechlorination of PCDD/Fs might be occurring, but the extent, if any, is very small. This low percentage probably explains why we did not find a factor related to microbial dechlorination when we conducted factor analysis on PCDD/F congeners alone in the water or sediment (data not shown). Because only the 2,3,7,8-substituted PCDD/Fs were measured in this data set, only the peri-dechlorination products could be observed. As we observed in our previous work, [3] evidence that microbial dechlorination occurs by this pathway suggests that the peri-lateral dechlorination pathway may also occur in this system.[11] In addition, microbial dechlorination products with fewer than four chlorines may also be present, but were not measured in these samples.

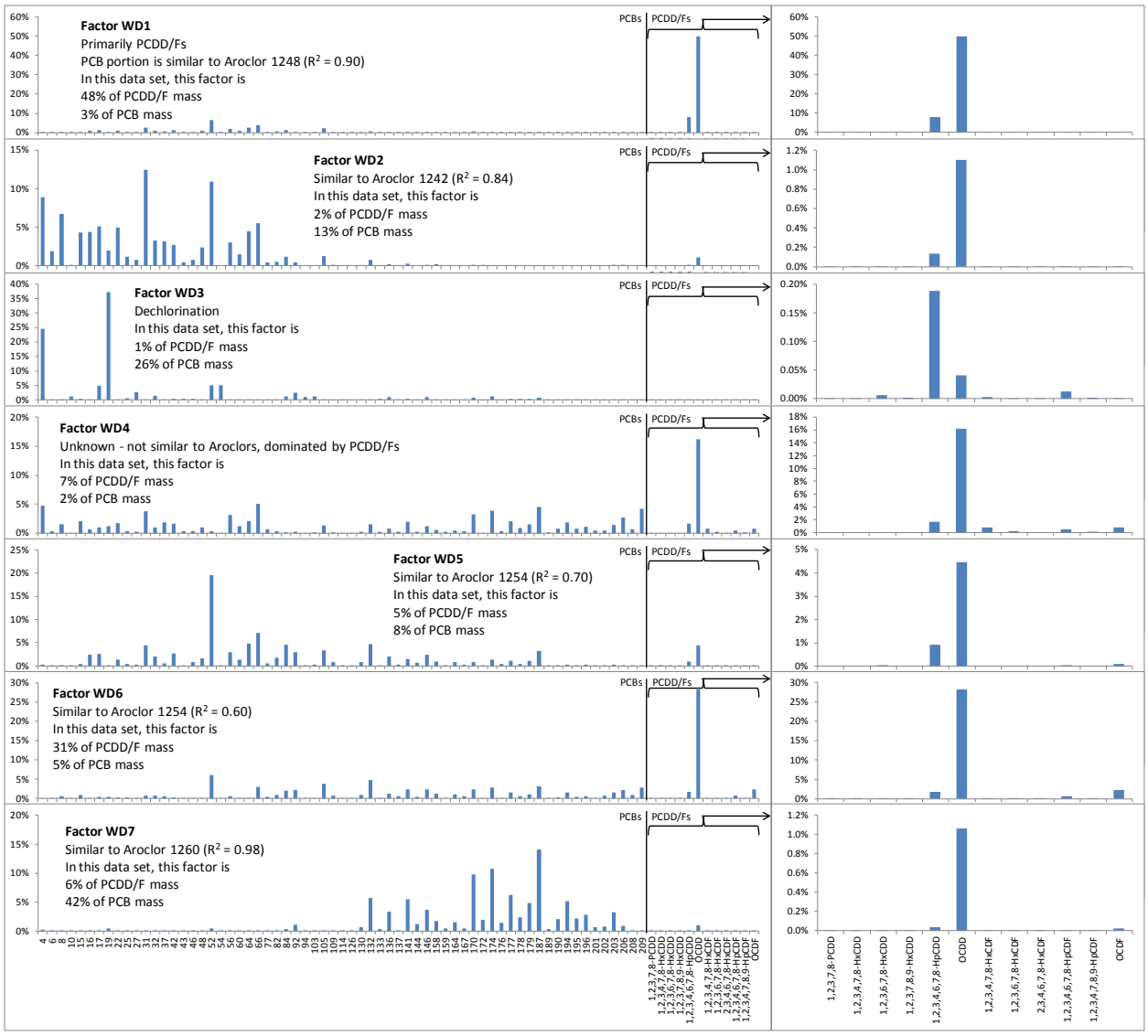

Figure S-3. Fingerprints resolved from the dataset on PCBs and PCDD/Fs in water in the Portland Harbor and interpretation of the factors based on similar to Aroclors. In the right panels, the y-axis is expanded where necessary to better visualize the PCDD/F portion of the fingerprint. Note that the % of the total mass in the data set represented by each factor is not a reliable indicator of the % of total PCBs in the water column, since this data set includes only a fraction of the PCBs measured.

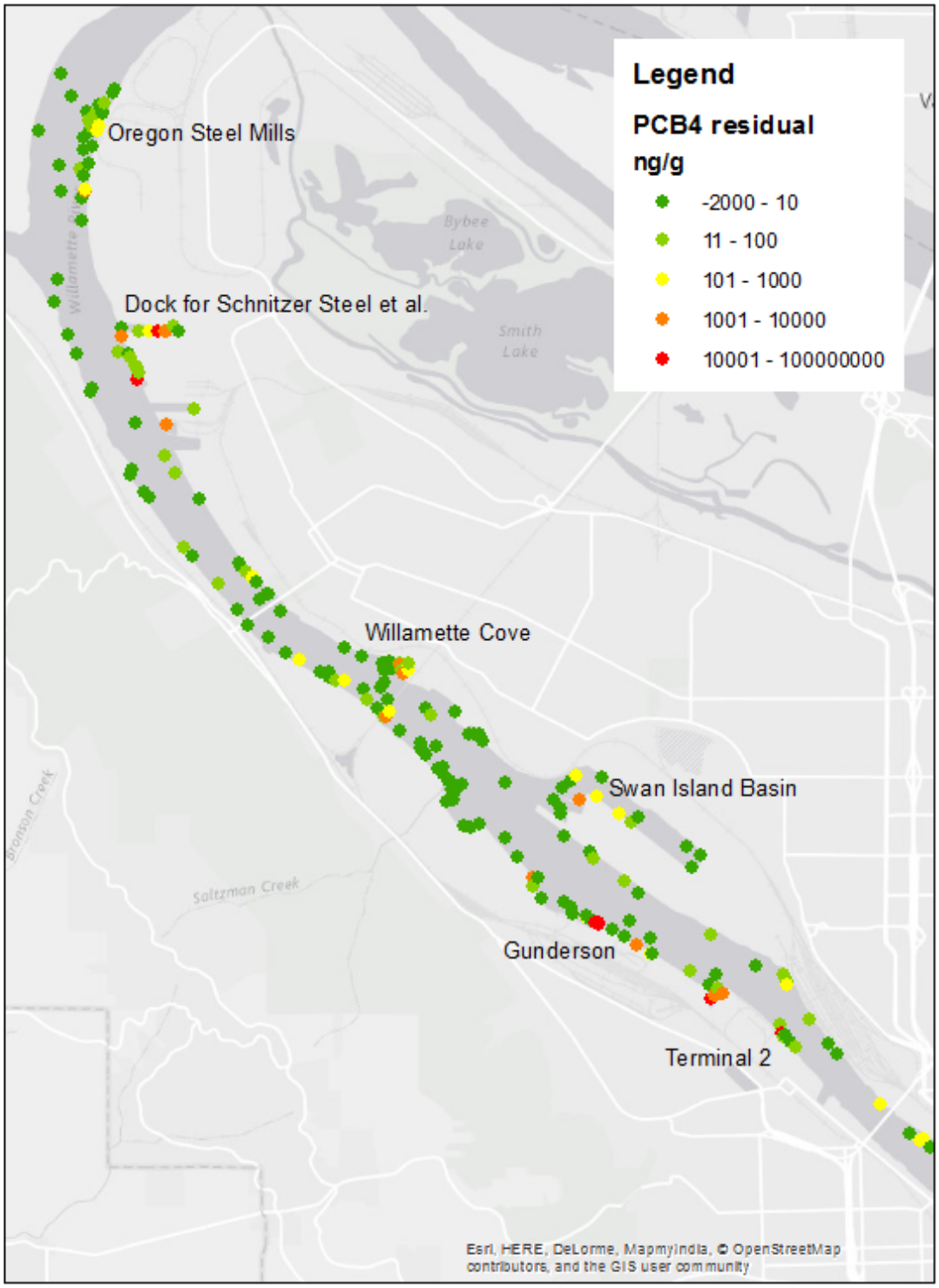

Figure S-4. Map of PCB 4 residual (measured minus modeled) in sediment.

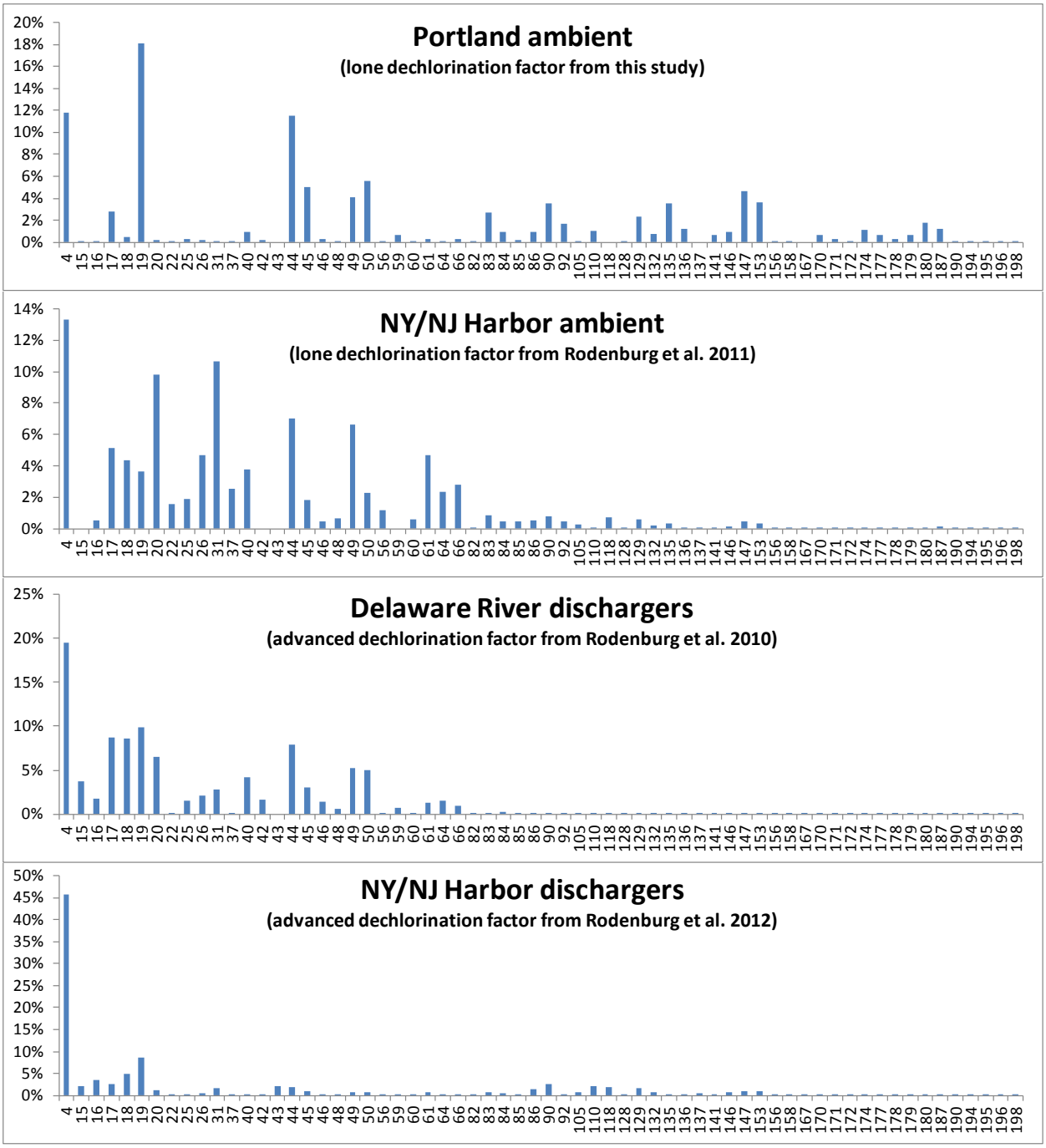

Figure S-5. Dechlorination factors resolved from factor analysis using various data sets. Because each data set utilized slightly different congener lists, only congeners common to all four data sets are shown. Note that co-eluting congeners are labeled using the lowest IUPAC congener number. All of these data sets utilized an SPB octyl GC column, so information about co-elutions is provided in Table S-1.

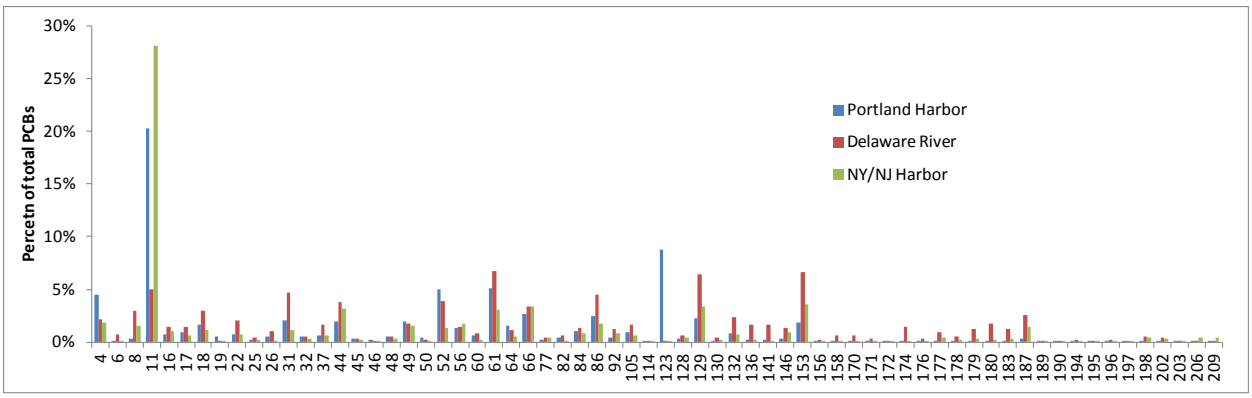

Figure S-6. PCB 11 dominated factors from the Portland Harbor ambient water (this study), the Delaware River ambient water [2], and the ambient water of the NY/NJ Harbor.[1] Because each data set utilized slightly different congener lists, only congeners common to all four data sets are shown. Note that co-eluting congeners are labeled using the lowest IUPAC congener number. All of these data sets utilized an SPB octyl GC column, so information about co-elutions is provided in Table S-1.

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